

IMPROVEMENT OF MAGNETIC PROPERTIES OF MnBi POWDERS PREPARED BY LOW-ENERGY BALL MILLING

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ABSTRACT

Recently MnBi magnetic material attracts a large attention due to its potential for high-temperature permanent magnetic applications. Although its spontaneous magnetization is moderate, $M_s \sim 74$ emu/g but its large coercivity, $H_c > 10$ kOe, which results in the theoretical value of energy product $(BH)_{max} \sim 16.8$ MGOe. The MnBi single phase is difficult to be prepared by using conventional techniques, such as the arc-melting, melt-spinning and sintering because of the big difference between the melting temperatures of Bi (544 K) and Mn (1519 K). Furthermore, the magnetic properties of magnets are strongly dependent on processing. The heat treatment of arc-melted alloys, the ball milling of annealed alloys, and the bulk magnets fabrication were found to have large effects on $(BH)_{max}$ of MnBi magnets. In this work, we report the effects of decomposition of MnBi low temperature phase (LTP) into Bi and Mn during low-energy ball milling (LEBM) carried out in xylene and silicon oil protection solvent environments and its influence on the magnetic properties of MnBi as-milled powders. In both solvents, by LEBM for 120 - 150 min, MnBi arc-melted and annealed alloys were ground into fine particles of 0.5 – 5 μm to increase H_c up to 5 kOe. By LEBM for 120 min, the viscous silicon oil constrained the decomposition of MnBi (LTP) keeping M_s around 56 emu/g instead of 42 emu/g of in-xylene LEBM powders.

Keywords: Low-energy ball milling (LEBM), xylene and silicon oil, MnBi powders, MnBi (LTP), magnetic properties.

1. INTRODUCTION

Nowadays, permanent magnets are continuously used in various applications like power generation, traction motor, DC motor, magnetic resonance imaging (MRI) technique, etc. [1-3]. It is accepted that the high performance of permanent magnets are usually due to the magnetism of the rare earth elements present in the composition of magnets. However, the 2011 rare earth supply crisis led to six-time price increase of Nd and Dy [4], two elements required for producing NdFeB-based magnets, make the development of rare-earth-free permanent magnets becoming important.

MnBi-based hard magnetic materials have been investigated since the early 1950s [5],

however over the past 60 years the quality of MnBi bulk magnets is restricted by the value of 8.4 MGOe [6] that is far below the theoretical limit of 16.8 MGOe [7]. The MnBi material owns the spontaneous magnetization M_s of ~ 74 emu/g, the high magneto-crystalline energy K_a of 0.9 MJ/m³, the elevated Curie temperature T_c of 360 °C and especially, the positive temperature coefficient of coercivity $d(iH_c)/dT > 0$. These features make MnBi-based magnets promising for high-temperature applications [8].

Commonly, to prepare the high-performance permanent magnets, the green magnetic powders (the as-milled powder used for magnet preparations) must be of high M_s and large iH_c . It has been observed [9-11] that the high-energy ball-milling process necessary to enhance coercivity iH_c is assisted by the reduction of M_s due to the decomposition of MnBi (LTP). Some other methods were also used to prepare high coercive MnBi green powders such as the mechanochemical synthesis method [12], direct chemical synthesis of MnBi particles [13]; but they are assisted by the low value of $M_s \sim 20$ emu/g.

The fact mentioned in previous publication [14] for preparing high-performance MnBi magnet show that the green MnBi powders have to own $M_s > 60$ emu/g and particle size must be about 500 nm to keep iH_c high.

In this paper, we report our investigation in preparing high-magnetization and submicron MnBi particles using low-energy ball milling (LEBM) in solvents of xylene and silicon oil.

2. EXPERIMENTAL

The alloys with nominal compositions of Mn₅₀Bi₅₀ were arc-melted from the starting high-purity 99.9 % metals Mn and Bi under argon atmosphere. The ingots were melted three times to ensure their homogeneity and annealed at 290 °C for 20 h in an argon flow. These pre-alloys were milled by LEBM technique functioned with 6 mm hard steel balls in appropriate solvents, namely xylene and silicon oil. The batch amount of pre-alloys was kept around 5 g, the weigh ratio of balls:powders was 10:1. The phases of pre-alloy and ball-milling powders were determined by using D8 advance Bruker X-ray diffractometer (XRD) with Cu-K α radiation with the scattering angle 2θ scan in the range from 20 to 80 degrees by the scanning step of 0.05° for 2 s. The phase composition and size crystallite were analyzed by means of Rietveld refinement of XRD patterns for all the diffraction peaks by using the Crystal Impact - Software for Chemists and Material Scientists and the method of the instant determination of MnBi (LTP) content presented in the previous work [15]. The morphology of powders was studied by using scanning electron microscopy (SEM). The hysteresis loops of prepared MnBi powders were measured by pulse field magnetometer (PFM) with the maximal magnetized magnetic field $H_{max} = 50$ kOe.

3. RESULTS AND DISCUSSION

Figure 1 plots the XRD pattern of the MnBi crushed arc-melted and annealed alloy before the milling process. All the peaks belong to the phases of Mn, Bi and MnBi. The main peaks of Bi(012) and LTP-MnBi(101) are located at 27.16 and 28.14 degrees, respectively. The MnBi (LTP) content calculated by Rietveld refinement equals 95 %wt. The main peak of Mn(411) at 43.02 degrees is not observable. The size of MnBi particles are about 10 ÷ 30 μ m as seen in the sketched SEM graph.

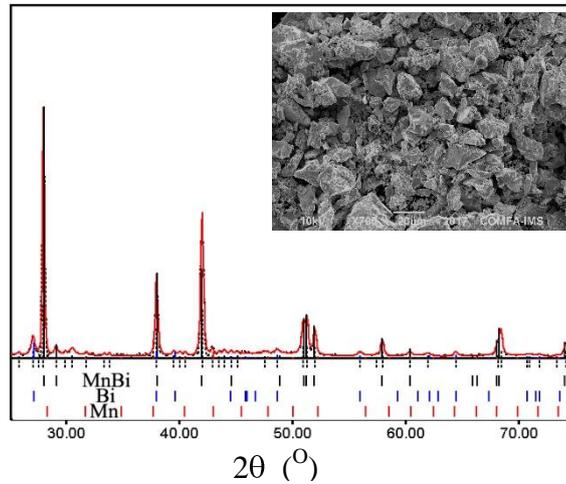


Figure 1. The XRD pattern treated by the Rietveld refinement procedure of the handily crushed arc-melted and annealed MnBi alloy. Its SEM graph is shown in the inset.

To prepare green powders for making magnets, the crushed powders were subjected to the in-solvent LEBM process. As a solvent, xylene is the first choice because of its anti-oxidation ability and relatively high boiling temperature ($\sim 140\text{ }^{\circ}\text{C}$).

The XRD patterns plotted in Fig. 2 show the milling-time dependent changes of the intensities of the diffraction peaks of MnBi and Bi. It is observed that the peak intensity ratio, $\alpha = I_{\text{MnBi}(101)}/I_{\text{Bi}(012)}$, decreases by increasing the milling time which corresponds with the decrease of MnBi LTP contents.

By using this ratio α and the method of the MnBi LTP content (γ) determination described in [15]. One estimates that the MnBi LTP of the powders milled for 0, 120 and 150 min are 95.0, 74.6 and 51 %wt, respectively.

$$\gamma = 44.6 + 51.3 \log \alpha$$

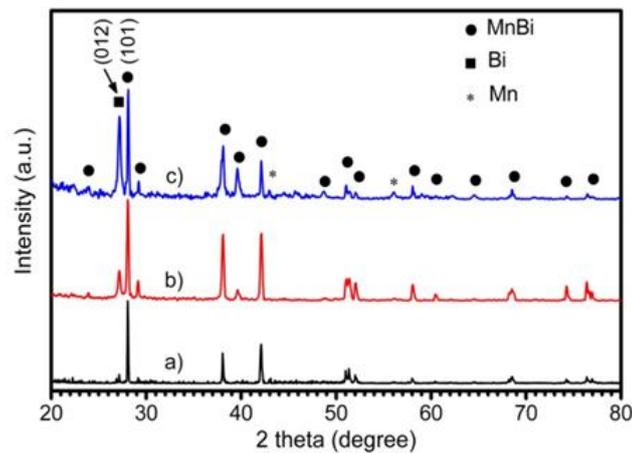


Figure 2. XRD patterns of MnBi in-xylene milling powders for: a) $t = 0$ min; b) $t = 120$ min; c) $t = 150$ min.

This MnBi (LTP) content reduction is caused by the decomposition of MnBi (LTP) into Bi and Mn phases leading to the observation of Mn peak located on the XRD pattern of the 150 min milling powders as seen on the curve c) of Fig. 2. It is worthy to note that the xylene solvent protects well the milling powders from the oxidation, so the XRD patterns are free of any peaks of Mn oxides which can be easily formed during the normal milling process.

The observed effect of the MnBi LTP decomposition is the main restriction causing the low performance of the milled MnBi powders. Once the milling process can not be skipped in order to increase H_c , the decomposition effect occurred during the milling reduces significantly M_s , so the green MnBi powders for making magnets are of low energy product $(BH)_{max}$.

This feature is reflected clearly on the Fig. 3, which plots the PFM-measured loops and the M_s as well H_c of the powder samples milled for 0 ÷ 180 min. After 180 min of milling, the coercivity H_c is increased from 2.1 to 5.8 kOe due to the refinement of the particle size from 20 μm to 1 μm as shown in Fig. 4. This coercivity enhancement is paid by the reduction of the magnetization M_s from 64 emu/g to around 30 emu/g.

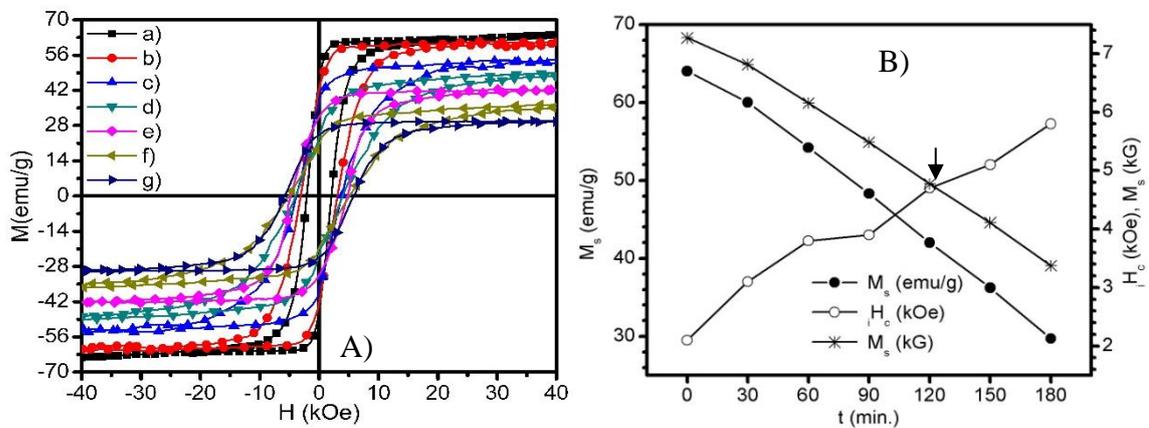


Figure 3. A) $M(H)$ loops of MnBi powders milled in xylene for: a) $t = 0$ min; b) $t = 30$ min; c) $t = 60$ min; d) $t = 90$ min; e) $t = 120$ min; f) $t = 150$ min; g) $t = 180$ min.

B) The summary of M_s in emu/g and in kG and H_c in kOe dependent on the milling times. The arrow indicates the balance point between $M_{s,b}$ and $H_{c,b}$.

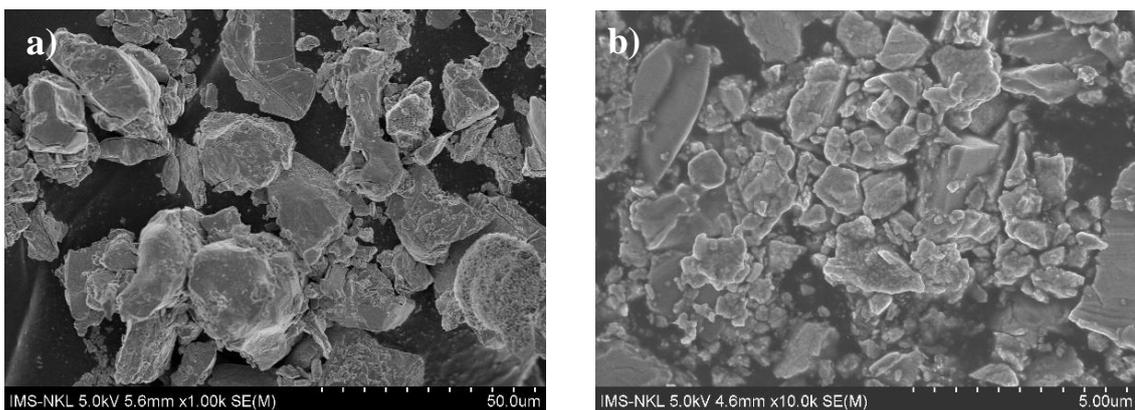


Figure 4. SEM images of MnBi powders milled in xylene for: a) $t = 0$ min; b) $t = 180$ min.

The $(BH)_{max}$ of milled powders is estimated by the model of single particle having the Rontghen mass density of 9.042 g/cm^3 of MnBi (LTP) phase; the perfect texture leading to the ratio $M_r = M_s$, where M_r is the remanent magnetization; the perfect squareness allowing ${}_bH_c = {}_iH_c$, where ${}_bH_c$ is the induction coercivity. In the framework of these suggestions, the energy product of powders is calculated as:

$$(BH)_{max} = (M_{s,b}(\text{kG}) \cdot {}_iH_{c,b}(\text{kOe})) / 4$$

here $M_{s,b}$ and ${}_iH_{c,b}$ are the balanced value of M_s and ${}_iH_c$ determined by their intersect as indicated by the arrow in Fig. 3(B) and the magnetization measured in emu/g has been converted into kG by using the above said mass density. This intersect point for the case of in-xylene LTBM powders corresponds to the milling time of 120 min. and the $(BH)_{max}$ of the milled powders is estimated equal $4.75 \text{ (kG)} \cdot 4.75 \text{ (kOe)} / 4 = 5.64 \text{ MGOe}$.

Although the mechanism of the decomposition effect is not understood, but it can be though that the mechanical energy of milling can give raise the motion of the Mn atoms inside the MnBi (LTP) unit cells thus disturbs the energy balance between Bi and Mn atoms leading to the release of Bi and Mn atoms from the unit cells of MnBi (LTP) to conserve the energy minimum state of the system.

To check this idea, the more viscous solvent as silicon oil was chosen to replace xylene. The optimal milling time was kept equal 120 min. The resultant powders have the morphology presented in Fig. 5. The milled particle size distribution has the peaked value at $1.5 \mu\text{m}$ with the long tail in the direction of big size.

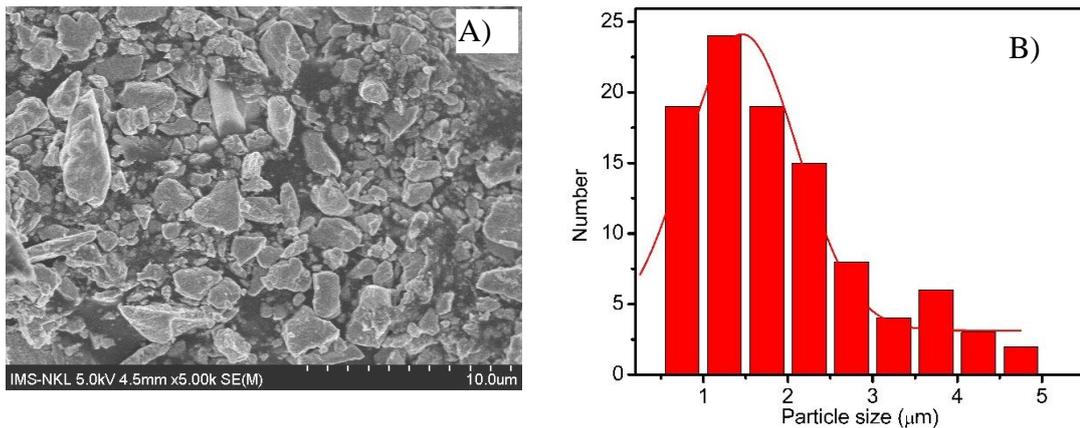


Figure 5. SEM image (A) and the particle distribution of MnBi powders after milling in silicon oil for $t = 120 \text{ min}$.

The quality of in-silicon-oil milled powders can be determined from the loops plotted on the Fig. 6. It was observed that the higher viscosity helped braking the decomposition process and kept M_s equal 5.45 kG after 150 min LTBM for reaching ${}_iH_c = 5 \text{ kOe}$. The milling time for reaching the balance between M_s and ${}_iH_c$ was shifted from the value of 120 min for the in-xylene LTBM powders to 160 min for the in-silicon-oil LTBM powders. The constrained decrease of M_s improved the performance of the in-silicon-oil LTBM powders with the balanced $M_{s,b} = 5.2 \text{ kG}$ and ${}_iH_c = 5.2 \text{ kOe}$, thus the $(BH)_{max}$ is up to 6.76 MGOe instead of 5.64 MGOe of the in-xylene LTBM powders.

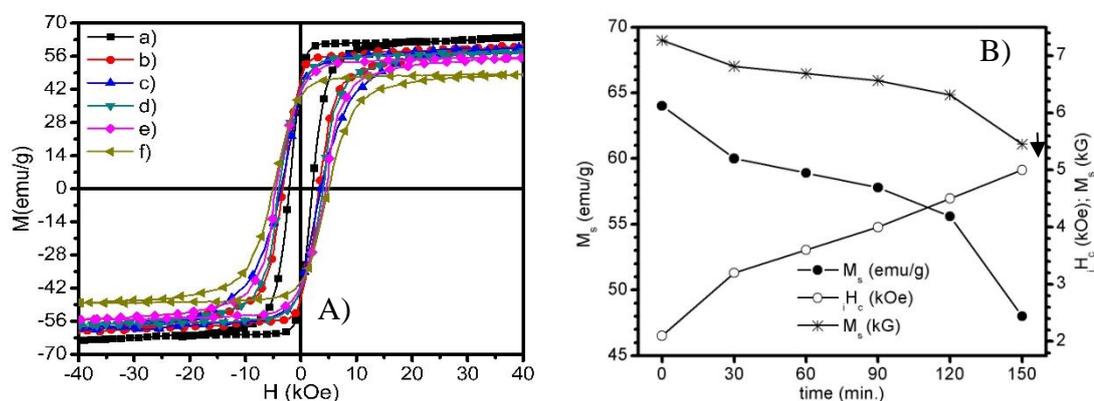


Figure 6. A) $M(H)$ loops of MnBi powders milled in silicon oil for: a) $t = 0$ min; b) $t = 30$ min; c) $t = 60$ min; d) $t = 90$ min; e) $t = 120$ min; f) $t = 150$ min; B) The summary of M_s and H_c dependent on the milling times. The arrow indicates the balance point between $M_{s,b}$ and $iH_{c,b}$.

4. CONCLUSION

In this paper, we have investigated the effect of the solvent (xylene and silicon oil) assisted low energy ball milling in preparing MnBi powders. As a rule, the ball-milling process is required for producing the highly coercive green compaction powders which will be used for making anisotropic bulk magnets. However, in the case of MnBi, the increase of coercivity caused by the milling process is paid by the decrease of the spontaneous magnetization due to the MnBi (LTP) decomposition effect. It has been shown that this MnBi (LTP) decomposition into Bi and Mn during the low energy ball-milling process is very crucial effect which decreases the MnBi (LTP) content reducing M_s and consequently $(BH)_{max}$ of green MnBi powders. This effect has been examined by milling in the different protection solvent environments such as xylene and silicon oil and revealed that the more viscous solvent can constrain the decomposition effect. So, for 120 min of milling, the optimal values of the coercivity iH_c and magnetization M_s achieved 4.5 kOe and 56 emu/g for in-silicon-oil LEBM in comparison with that of 4.8 kOe and 42 emu/g for in-xylene LEBM powders. The constrained reduction of M_s improved the balance between M_s and iH_c leading to improved $(BH)_{max}$ of in-silicon-oil LEBM powders. We believe that the LEBM combined with the suitable viscous and low temperature milling solvent are the key for further improvement of the quality of the massive production green MnBi powders.

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REFERENCES

1. McCallum R. W., Lewis L. H., Skomski R., Kramer M. J., Anderson I. E. - Practical Aspects of Modern and Future Permanent Magnets, Annual Review of Materials Research **44** (2014) 451-477.

2. Laura Menini, Corrado Possieri, Antonio Tornambè - Application of algebraic geometry techniques in permanent-magnet DC motor fault detection and identification, *European Journal of Control* **25** (2015) 39-50.
3. John V. M. Mcginley, Mihailo Ristic, Ian R. Young - A permanent MRI magnet for magic angle imaging having its field parallel to the poles, *Journal of Magnetic Resonance* **271** (2016) 60-67.
4. Ding Kaihong - The Rare Earth Magnet Industry and Rare Earth Price in China, *EPJ Web of Conferences* **75** (2014) 3 pages.
5. Adams E., Hubbard W. M., Syeles A. M. - A New Permanent Magnet from Powdered Manganese Bismuth, *J. Appl. Phys.* **23** (1952) 1207 - 1211.
6. Van Vuong Nguyen, Poudyal N., Xubo Liu, Liu J. P., Kewei Sun, Kramer M. J., Cui Jun - High-Performance MnBi Alloy Prepared Using Profiled Heat Treatment, *IEEE Transactions on Magnetics* **50** (2014) 1-6.
7. Cui J., Choi J. P., Li G., Polikarpov E., Darsell J., Overman N., Olszta M., Schreiber D., Bowden M., Droubay T., Kramer M. J., Zarkevich N. A., Wang L. L., Johnson D. D., Marinescu M., Takeuchi I., Huang Q. Z., Wu H., Reeve H., Vuong N. V., Liu J. P. - Thermal stability of MnBi magnetic materials, *Journal of Physics: Condensed Matter* **26** (2014) 064212.
8. Coey J. M. D. - New permanent magnets; manganese compounds, *Journal of Physics: Condensed Matter* **26** (2014) 064211.
9. Kanari K., Sarafidis C., Gjoka M., Niarchos D., Kalogirou O. - Processing of magnetically anisotropic MnBi particles by surfactant assisted ball milling, *Journal of Magnetism and Magnetic Materials* **426** (2017) 691-697.
10. Rama Rao N. V., Hadjipanayis G. C. - Influence of jet milling process parameters on particle size, phase formation and magnetic properties of MnBi alloy, *Journal of Alloys and Compounds* **629** (2015) 80-83.
11. Sumin Kim, Hongjae Moon, Hwaebong Jung, Su-Min Kim, Hyun-Sook Lee, Haein Choi-Yim, Wooyoung Lee - Magnetic properties of large-scaled MnBi bulk magnets, *Journal of Alloys and Compounds* **708** (2017) 1245-1249.
12. Rama Rao N. V., Gabay A. M., Hu X., Hadjipanayis G. C. - Fabrication of anisotropic MnBi nanoparticles by mechanochemical process, *Journal of Alloys and Compounds* **586** (2014) 349-352.
13. Rowe Michael, Skoropata E., Wrocynskyj Y., Desautels Ryan, Van Lierop Johan - MnBi nanoparticles: Improved magnetic performance through annealing of as-synthesized nanoparticles, 2015 (1-2).
14. Xie Wei, Polikarpov Evgueni, Choi Jung-Pyung, Bowden Mark E., Sun Kewei, Cui Jun - Effect of ball milling and heat treatment process on MnBi powders magnetic properties, *Journal of Alloys and Compounds* **680** (2016) 1-5.
15. Truong Xuan Nguyen and Vuong Van Nguyen - Preparation and Magnetic Properties of MnBi Alloy and its Hybridization with NdFeB, *Journal of Magnetism* **20** (2015) 336-341.